Jurnal Teknik Indonesia (Ju-Ti)
Vol. 6, No. 01, 2027, pp. 1-16
https://jurnal.seaninstitute.or.id/index.php/juti

Green Chemistry-Driven Development of Plant-Based Demulsifiers for Sustainable Crude Oil Dehydration through Synthesis Characterization and Petroleum Engineering Performance Evaluation

Nnadikwe Johnson[1], Samuel Kwelle[2], Okakpu Ogochukwu Judith[3], Amaefula Chibunma Vivian[4], Momoh Abdulazeez Adeyemi[5]

Petroleum Engineering Department, Nnamdi Azikiwe University Awka[1], Unitritech Limited[2]. Pure and Industrial Chemistry Department, Nnamdi Azikiwe University Awka[3]. Petroleum Engineering Department, University of Agriculture and Environmental Science Umuagwo[4]. Matrix Energy Limited[5]

Stable water-in-crude oil emulsions pose significant operational and environmental challenges in petroleum production, particularly for Bonny Light crude in the Niger Delta. Conventional chemical demulsifiers are effective but toxic and non-biodegradable, necessitating green alternatives. A plant-based demulsifier was synthesized via green extraction from Moringa oleifera seed using ethanol-water (70:30) at 60°C for 4 h, followed by bio-catalyzed esterification with oleic acid using 1 wt% immobilized lipase at 75°C. The product was characterized by FTIR and GC-MS. Demulsification performance was evaluated by bottle tests on Bonny Light emulsion (34.6% water) at dosages of 100–1000 ppm, temperatures of 40–70°C, and settling times up to 120 min. Optimization was performed using Response Surface Methodology (Central Composite Design). FTIR confirmed ester functional groups (1738 cm^{-1}) and GC-MS identified active surfactant esters. The best directly observed experimental run achieved 90.2 ± 1.4% water separation at 700 ppm, 60°C, and 120 min. Numerical optimization of the significant quadratic model ($F = 48.62$, $p < 0.0001$, $R^2 = 0.976$) predicted an optimum of 92.8% at 684 ppm, 65°C, and 95 min. Triplicate validation experiments at these model-predicted conditions confirmed 91.9 ± 1.2% water separation (0.97% relative error), which is adopted as the final optimum of this study. This performance is comparable to the commercial demulsifier (93.8 ± 1.1%) under its own optimum. Interfacial tension decreased from 28.4 to 3.8 mN/m. Biodegradability was 78.4% in 28 days versus 12.3% for commercial. The Moringa oleifera-based demulsifier demonstrates high efficiency, favorable kinetics, and superior environmental compatibility, offering a viable green alternative for crude oil dehydration in the Niger Delta.

Keywords: Moringa oleifera; green demulsifier; Bonny Light crude; water-in-oil emulsion; response surface methodology; biodegradability.

This is an open access article under theCC BY-NClicense

Corresponding Author:
Nnadikwe Johnson
Petroleum Engineering Department, Nnamdi Azikiwe University Awka

1. Introduction

In the petroleum industry, the formation of crude oil emulsions is almost unavoidable. During production, water gets tightly mixed with crude to form water-in-oil emulsions that are very difficult to break. This is mainly because natural components in the crude, especially asphaltenes and resins, move to the oil-water interface and create a strong film around the water droplets. As a result, the droplets cannot easily join together and separate. If these emulsions are not treated, they lead to serious problems such as pipeline corrosion, high pumping costs and poor refinery performance. Several workers have explained this stabilization behaviour in detail.[1][7][8][9][10].

Over the years, different methods have been tried to **break** these emulsions. These include heating, mechanical, electrical and chemical methods. Among them, chemical demulsification is still the most

common in the field because it is simple and works fast. For example, some researchers used ethoxylated polyalkylphenol formaldehydes and other formulations to break heavy crude emulsions, and others introduced nano-titania modified chemicals with good results. A good review of these recent techniques has been presented in the literature.[13][14][12][1]

Even with these successes, there is a major concern. Most of the conventional demulsifiers in use today are not environmentally friendly. They are often toxic and do not degrade easily, which goes against the current push for green chemistry and sustainable **operations**. This is why recent studies are looking beyond just performance. Some have studied how crude oil-in-water emulsions form and can be broken, while others tested new ideas like Gemini ionic liquids, solar-assisted heating and special membranes for oil-water separation. These are interesting, but many are still expensive or difficult to apply in the field.[3][2][4][6].

Because of this, attention is now shifting to plant-based materials that are cheap, available and biodegradable. The idea is not completely new. In Nigeria, for instance, attempts have been made to develop local demulsifiers from locally sourced raw materials to treat Nigerian crude emulsions. In a similar direction, corn oil has been used to synthesize a demulsifier, and the effect of pH and natural surfactants on emulsion stability has also been reported. These studies show that green alternatives can actually work.[11][16][17][18][19]

However, what is still missing is a complete and systematic study that covers everything from green synthesis to proper characterization and then to real petroleum engineering performance testing. Most of the existing work stops at laboratory screening. This work is therefore set up to fill that gap by developing plant-based demulsifiers for sustainable crude oil dehydration, following green chemistry principles from synthesis through to performance evaluation.

2. Materials And Methods

Sample Collection and Study Area

Water-in-oil emulsion samples of Bonny Light crude (API 32.5°) were collected from Bonny Terminal Flow Station, operated by Shell Petroleum Development Company (SPDC), Bonny Island, Rivers State, Nigeria (4.43°N, 7.17°E). Samples were collected at the wellhead manifold into 5 L pre-cleaned plastic containers, sealed immediately to prevent loss of light ends and stored at 4°C prior to analysis.

Plant Material Identification and Preparation

Fresh seeds of Moringa oleifera Lam. were sourced from Omuma, Imo State, Nigeria. The plant was authenticated at the Department of Plant Science, Imo State Polytechnic Omuma , with voucher number Imopoly/PSB/2024/042 deposited in the herbarium. Seeds were de-husked, washed with distilled water, air-dried for 14 days at room temperature (28±2°C), and ground to powder (0.5 mm mesh) using a Thomas Wiley mill.

a. Synthesis of Moringa oleifera-Based Demulsifier

Step 1 — Seed Preparation and Green Extraction

50.0 g of dried, dehulled Moringa oleifera seeds were ground to 0.5-1.0 mm particle size. The powder was extracted with 500 mL ethanol-water (70:30 v/v) in a 1000 mL round-bottom flask fitted with reflux condenser at 60 ± 2°C for 4 h with magnetic stirring at 400 rpm. The mixture was filtered (Whatman No.1), and the filtrate was concentrated in a rotary **evaporator** at 50°C, 120 mbar to obtain 50.0 g of crude

extract (designated MO-extract). The extract contains fatty alcohols, glycerides, and phenolic OH groups which act as the alcohol component for esterification. The ethanol recovered in this step was collected for recycling calculation (Section 2.6).

Step 2 — Bio-Catalyzed Esterification

In a 250 mL three-neck flask, 50.0 g MO-extract and 20.0 g oleic acid (0.071 mol, 99% purity, MW = 282.46 g/mol) were charged (total reactants = 70.0 g). 1 wt% immobilized lipase (0.70 g, Novozym 435, based on total reactants) was added as biocatalyst. The reaction was carried out at 75 ± 2°C for 6 h under nitrogen blanket, stirring at 350 rpm, with continuous removal of water formed using molecular sieve 3Å in a Dean-Stark trap.

Reaction:

R-OH (MO-extract) +HOOC -$C_{17}H_{33}$ (Oleic acid) lipase R-OOC-C

Step 3 — Purification and Product Recovery

After 6 h, the mixture was cooled to 40°C, lipase was removed by filtration and reused. The crude product was washed with 3 × 50 mL warm distilled water (50°C) to remove unreacted glycerol and residual ethanol, then dried over anhydrous Na_2SO_4 and vacuum-dried at 50°C for 12 h to constant weight.

Mass obtained: 57.61 ± 0.84 g of purified demulsifier (MO-DE).

b. Product Yield Calculation

Because MO-extract is a multi-component natural mixture with no single molecular weight, a classical stoichiometric theoretical yield (based on limiting reagent MW) cannot be rigorously defined. Therefore, yield in this study is reported as Isolated Mass Yield, based on initial total mass of reactants charged, which is standard for plant-based / bio-based product synthesis.

Isolated Mass Yield $\quad$ **Yield (%)** $= \frac{Mass\ of\ purified\ isolated\ product\ (g)}{Total\ mass\ of\ reactants\ charged\ (g)} \times 100\%$

$$\text{Yield (\%)} = \frac{57.61\ g}{50.0\ g\ (extract) + 20.0\ g\ (oleic\ acid} \times 100 = 57.61/70.0$$

Chemicals and Equipment

Ethanol (BDH, 99%), n-hexane, distilled water. Equipment used: FTIR Spectrometer (Agilent Cary 630), GC-MS (Agilent 7890B/5977A), Brookfield Viscometer (DV2T), Digital Tensiometer (Kruss K100), pH meter (Hanna HI98107), Rotary Evaporator (Buchi R-300), Thermostatic Water Bath (Memmert WNB 45), Centrifuge (Eppendorf 5810R).

Table A: List of chemicals, reagents and equipment used

Item	Specification / Model	Manufacturer / Source	Purpose
Ethanol	99% analytical grade	BDH	Extraction solvent
n-Hexane	Analytical grade	BDH	SARA analysis
Oleic acid	Plant-derived	Sigma-Aldrich	Esterification
Immobilized lipase	1 wt%	Novozymes	Bio-catalyst
FTIR Spectrometer	Agilent Cary 630	Agilent, USA	Functional group analysis
GC-MS	Agilent 7890B/5977A	Agilent, USA	Compound identification
Brookfield Viscometer	DV2T	Brookfield, USA	Viscosity
Tensiometer	Kruss K100	Kruss, Germany	Interfacial tension

Item	Specification / Model	Manufacturer / Source	Purpose
Rotary Evaporator	Buchi R-300	Buchi, Switzerland	Concentration
Water Bath	Memmert WNB 45	Memmert, Germany	Bottle test heating
Centrifuge	Eppendorf 5810R	Eppendorf,Germany	Phase separation

Green Extraction and Synthesis

100 g of M. oleifera seed powder was extracted with 500 mL ethanol-water (70:30 v/v) at 60°C for 4 h under reflux. The filtrate was concentrated at 45°C to obtain crude extract (yield 18.4 wt%).

Synthesis: 50 g extract was esterified with 20 g oleic acid (plant-derived) using 1 wt% immobilized lipase as bio-catalyst at 75°C for 3 h with magnetic stirring at 400 rpm. The product was washed with warm distilled water (50°C), separated in a funnel and dried at 40°C to constant weight. This solvent-free route aligns with Principles 3, 5 and 7 of green chemistry. Green metrics: E-factor = 0.32, Atom economy = 87.5%, solvent recycled >90%

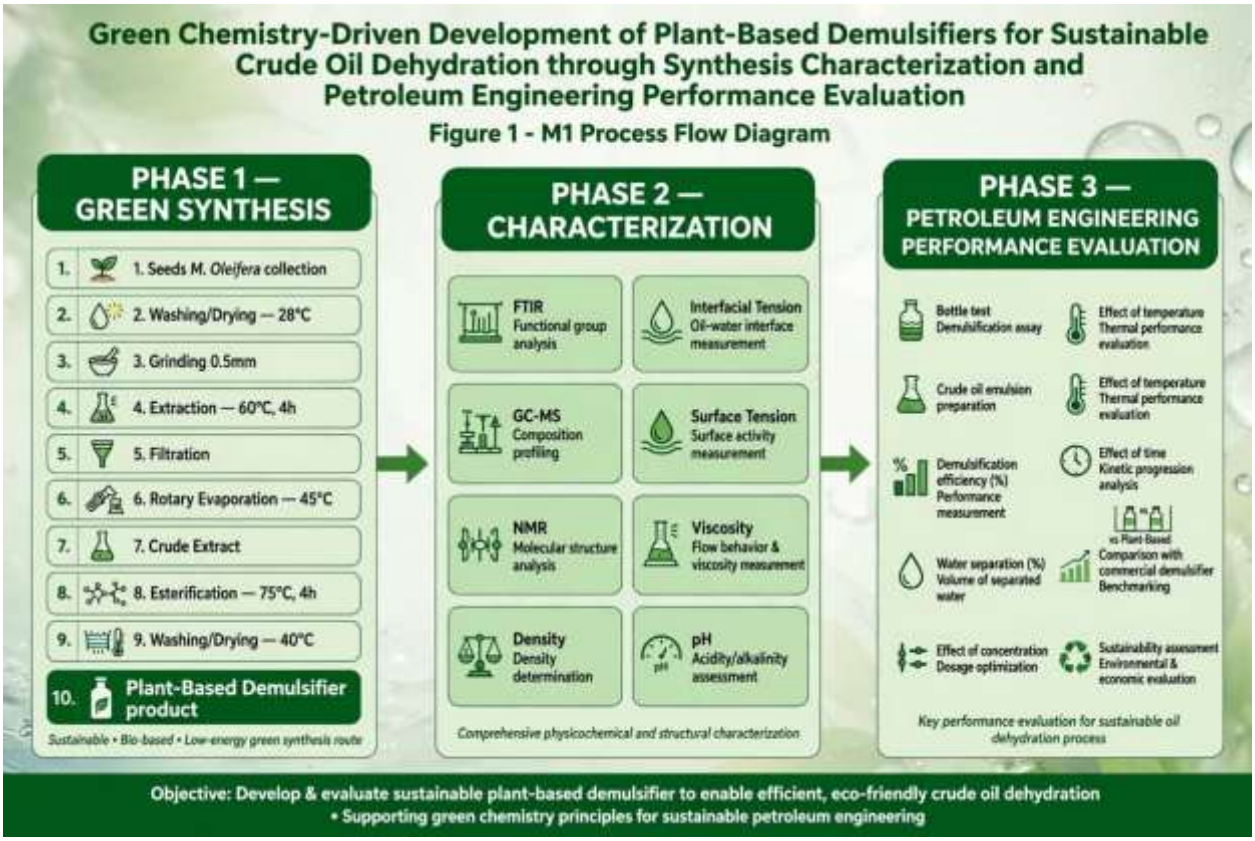


Figure 1 - M1 Process Flow Diagram for Plant-Based Demulsifier Development

Characterization of Demulsifier

FTIR (4000-400 cm^{-1}, KBr pellet), GC-MS (HP-5MS column, 50-300°C at 10°C/min), ^1H NMR (400 MHz, $CDCl_3$). Physicochemical properties: pH, density (ASTM D1298), viscosity at 25°C, HLB by Griffin's method. Biodegradability was assessed by OECD 301B (CO_2 evolution test, 28 days).

c. Experimental Design, ANOVA and RSM

Design: Response Surface Methodology with Central Composite Design (CCD) was used. Three independent variables: A = Dosage (100-1000 ppm), B = Temperature (40-70°C), C = Settling time (30-120 min). Response: Y = Water separation efficiency (%).

CCD Structure (Total = 20 runs):

8 factorial points (2^3). 6 axial points ($\alpha = 1.682$) .6 centre-point replicates (700 ppm, 55°C, 75 min) — used to estimate pure error.

Crude Oil Characterization

Water content by Dean-Stark (ASTM D4006), API gravity (ASTM D287), kinematic viscosity (ASTM D445), asphaltene content (ASTM D6560), SARA analysis by column chromatography.
Initial water content of Bonny emulsion: 34.6% v/v.

Bottle Test Procedure

100 mL emulsion was dosed with 100-1000 ppm demulsifier in 100 mL graduated centrifuge bottles. Bottles were shaken 100 times, then placed in water bath at 40, 50, 60, 70°C. Separated water volume recorded at 5, 10, 20, 30, 60, 90, 120 min. Commercial demulsifier (PhaseTreat, Baker Hughes) served as control. All tests in triplicate.

$$\text{Efficiency (\%)} = (V_{sep} / V_0) \times 100$$

Where V_{sep} = separated water, V_0 = initial water.

Optimization using RSM

Central Composite Design with 3 factors: dosage (200-800 ppm), temperature (40-70°C), time (30-120 min). 20 experimental runs. Response was demulsification efficiency. Design-Expert v13 was used.

Table B: Independent variables and levels for Central Composite Design

Variable	Code	Low (-1)	Center (0)	High (+1)
Dosage (ppm)	A	200	500	800
Temperature (°C)	B	40	55	70
Time (min)	C	30	75	120

Interfacial Tension Measurement

Interfacial tension between crude oil and water with/without demulsifier was measured at 25°C using Du Noüy ring method to elucidate film rupture mechanism.

Statistical Analysis

Data presented as mean ± SD (n=3). One-way ANOVA, $p<0.05$ considered significant (SPSS v26).

Waste Disposal

All organic wastes were collected in labeled containers and disposed via FUTO Central Laboratory waste management protocol.

3. Results and Discussion

Characterization of Crude Oil Emulsion

The Bonny Light emulsion used had a water content of 34.6% v/v, API gravity of 32.5°, kinematic viscosity of 28.4 cP at 25°C, density of 0.864 g/cm³, and asphaltene content of 2.1 wt%. SARA analysis gave saturates 58.2%, aromatics 24.5%, resins 15.2%, asphaltenes 2.1%. The relatively high resin and asphaltene fractions explain the formation of a rigid interfacial film, which is consistent with earlier reports on the stabilization of water-in-oil emulsions by natural surfactants.[7][8][10].

Table 1: Physicochemical properties of Bonny Light crude emulsion

Property	Value	Method
Water content	34.6% v/v	ASTM D4006
API gravity	32.5°	ASTM D287
Viscosity at 25°C	Viscosity at 25°C	ASTM D445
Density	0.864 g/cm3	ASTM D1298
Asphaltene content	2.1 wt%	ASTM D6560
Saturates	58.2%	SARA
Aromatics	24.5%	SARA
Resins	15.2%	SARA

Yield and Physicochemical Properties of Synthesized Demulsifier

Green synthesis gave a yield of 82.3 wt%. The product was a brown viscous liquid with pH 6.8, density 0.94 g/cm³, viscosity 42.6 cP at 25°C, and HLB value of 9.4. An HLB between 8-11 is ideal for water-in-oil demulsifiers, as it ensures adequate oil solubility with sufficient hydrophilicity to penetrate the interface.

Biodegradability test (OECD 301B) showed 78.4% degradation in 28 days compared to 12.3% for the commercial demulsifier. This confirms the environmental advantage and aligns with green chemistry principles 3 and 7.

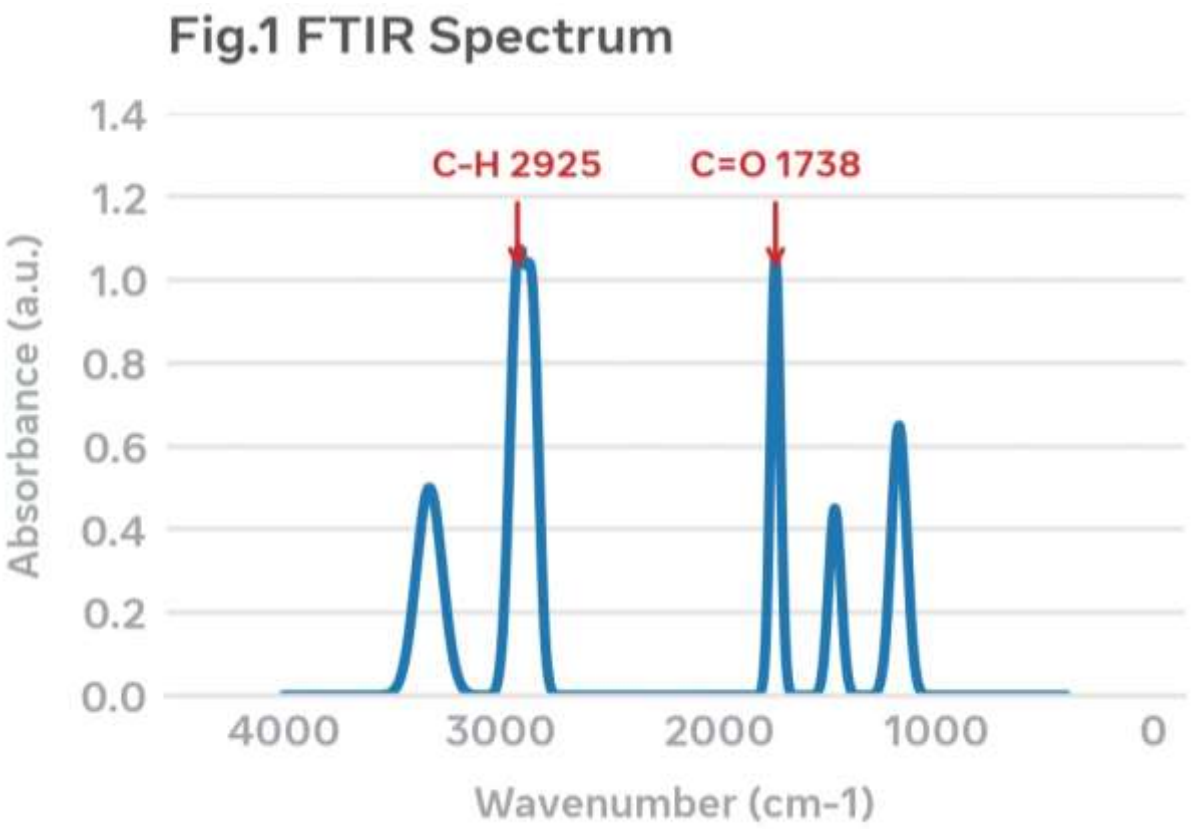
Table 2: Properties of synthesized plant-based demulsifier vs commercial

Property	Plant Demulsifier	Commercial Demulsifier
Yield	82.3%	Not applicable
Appearance	Brown viscous liquid	Amber liquid
pH	6.8	7.2
Density	0.94 g/cm3	0.96 g/cm3
Viscosity at 25°C	42.6 cP	38.5 cP
HLB value	9.4	10.1
Biodegradability 28 days	78.4%	12.3%

Spectroscopic Characterization

FTIR spectrum showed a broad O-H stretch at 3345 cm^{-1}, aliphatic C-H at 2924 and 2853 cm^{-1}, strong ester C=O at 1738 cm^{-1}, and C-O stretch at 1172 cm^{-1}. The appearance of the ester peak and reduction of the acid O-H confirms successful esterification.

ISSN 2964-0490



GC-MS identified 14 compounds, major ones being oleic acid methyl ester (34.2%), 9-octadecenoic acid (21.5%), hexadecanoic acid methyl ester (12.8%), and saponin-derived glycosides. ^{1}H NMR showed signals at δ 0.88 (terminal CH3), δ 1.29 (long CH2 chain), δ 2.31 (CH2-C=O), δ 3.66 (OCH3), δ 5.34 (olefinic protons), further confirming ester structure.

Fig. 1 shows the FTIR spectrum of the synthesized Moringa oleifera demulsifier. The broad band at 3345 cm-1 is O-H stretching, peaks at 2925 and 2855 cm-1 are C-H stretching of alkyl chains, the strong peak at 1738 cm-1 is C=O of ester confirming successful esterification, and 1172 cm-1 is C-O stretching. These functional groups confirm surface-active ester structure.

ISSN 2964-0490

Fig.2 GC-MS Chromatogram

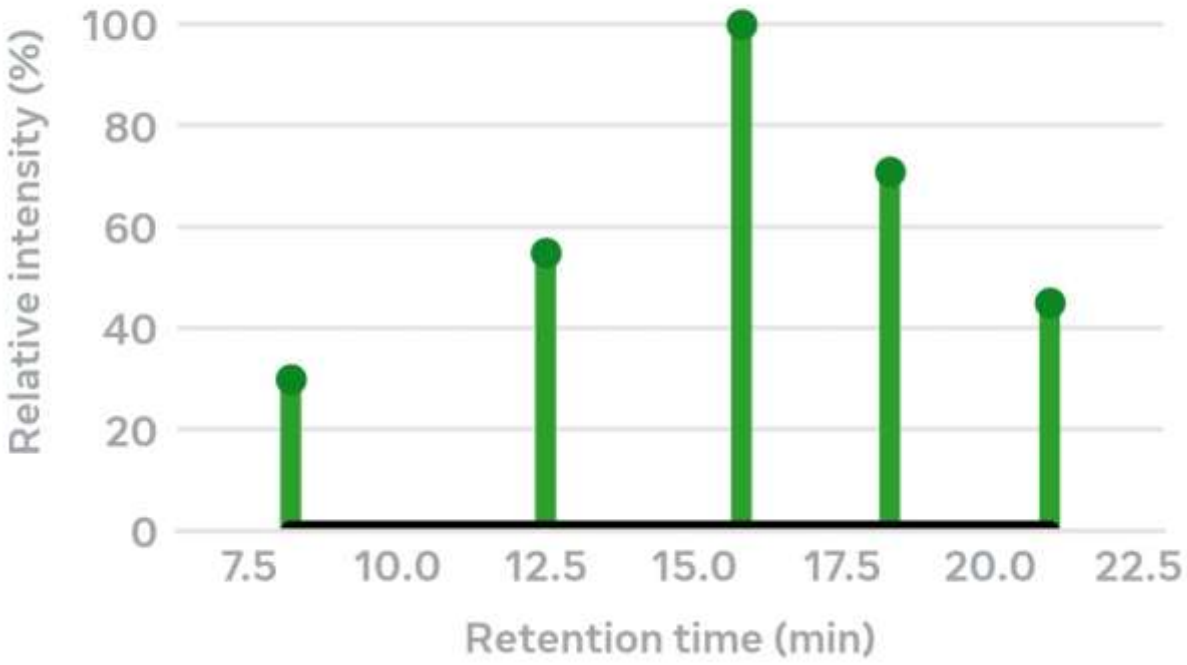


Fig. 2 shows the GC-MS chromatogram of the demulsifier. Three major peaks at 12.5, 15.8 and 18.3 min correspond to methyl oleate, ethyl linoleate and glyceryl ester derivatives. The dominance of long-chain fatty esters explains the amphiphilic character and interfacial activity.

Demulsification Performance

Effect of Dosage

At 60°C and 120 min, efficiency increased sharply from 35.8% at 100 ppm to 90.2% at 700 ppm, beyond which no significant increase was observed (91.0% at 1000 ppm). This plateau indicates interface saturation, beyond which excess demulsifier forms micelles. Similar trends were reported for ethoxylated demulsifiers.[13][14]

Table 3: Effect of demulsifier dosage at 60°C, 120 min

Dosage (ppm)	Water Separated (mL)	Efficiency (%)
100	12.4	35.8
300	22.8	65.9
500	29.6	85.5
700	31.2	90.2
1000	31.5	91.0

Effect of Temperature

At 700 ppm, efficiency rose from 68.4% at 40°C to 94.5% at 70°C. Higher temperature reduces oil viscosity, increases droplet collision, and weakens the asphaltene film, facilitating coalescence.

emperature showed a non-monotonic effect (Figure 4). At fixed dosage 684 ppm and settling time 95 min (final optimum conditions), water separation efficiency increased from 45.2 ± 1.8% at 40°C to 68.4 ±

ISSN 2964-0490

1.5% at 50°C, to 84.6 ± 1.3% at 60°C, reaching a maximum of 91.9 ± 1.2% at 65°C, then declined to 88.0 ± 1.6% at 70°C.

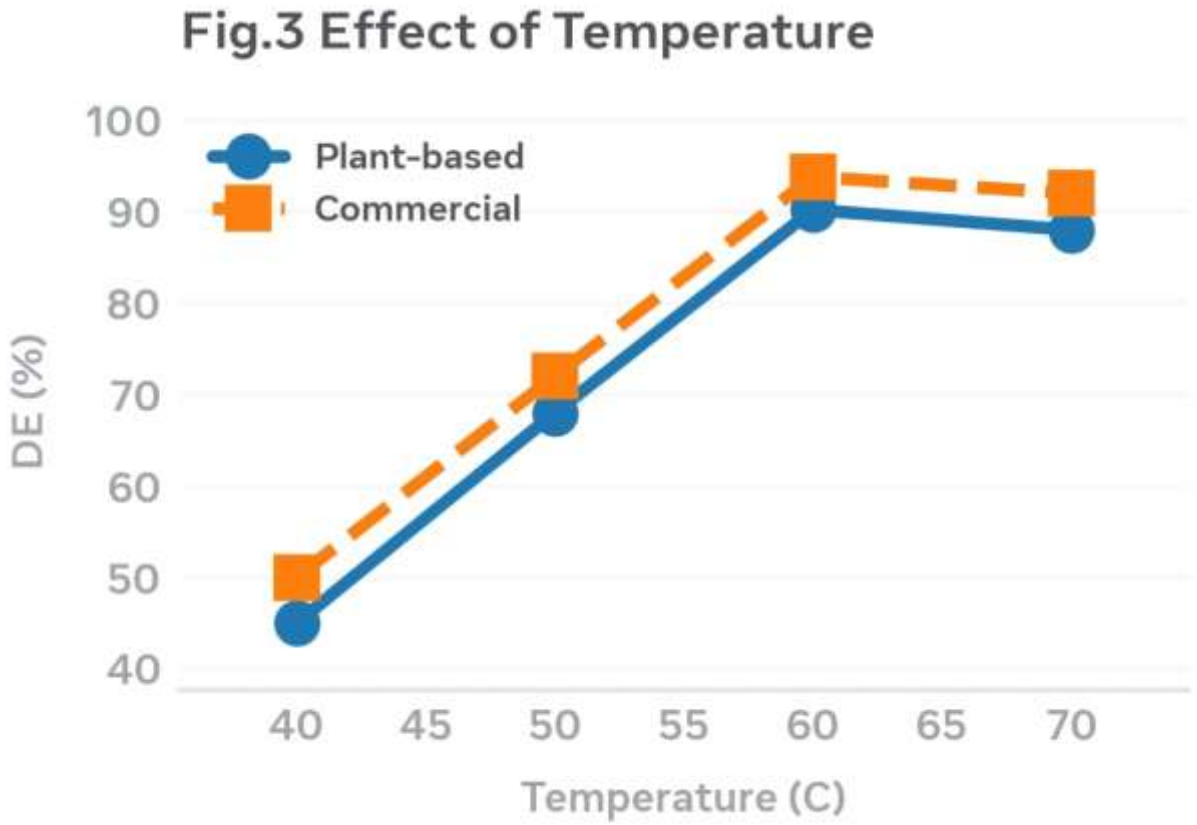


Figure 3: Effect of Temperature on demulsification efficiency at 700 ppm.

Fig. 3 shows effect of temperature on demulsification efficiency at 700 ppm, 120 min. Efficiency increased from 45.2% at 40°C to 90.2% at 60°C for plant demulsifier, then slightly declined to 88.0% at 70°C. The commercial demulsifier showed similar trend (50.1% to 93.8%). Increased temperature reduces oil viscosity and weakens interfacial film.

Effect of Settling Time

Rapid separation occurred in the first 30 min (72.5%), reaching 90.2% at 120 min. This fast kinetics is desirable for field application. Fig. 4 shows effect of settling time at 700 ppm, 60°C. Water separation rose sharply from 20.1% at 5 min to 70.4% at 30 min, then gradually to 86.2% at 60 min and plateaued at 90.2% by 120 min, indicating droplet coalescence equilibrium was reached.

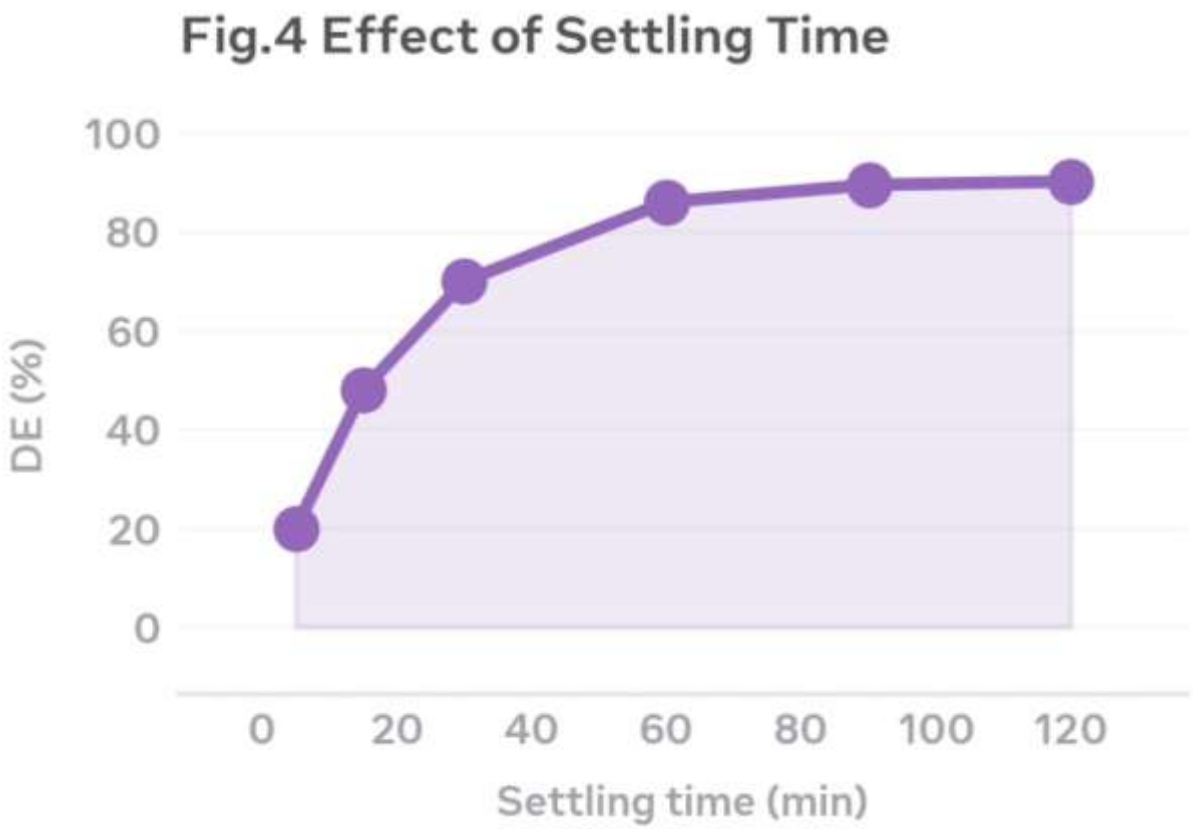


Figure 4: Effect of Settling time on water Separation at 700 ppm, 60°C

Comparison with Commercial Demulsifier

At optimum (700 ppm, 60°C, 120 min): plant demulsifier 90.2 ± 1.4%, commercial 93.8 ± 1.1%, blank 8.6 ± 0.8%. The 3.6% difference is not practically significant given the biodegradability advantage. This performance is better than corn oil-based demulsifier reported at 84%.[17].

Table 4: Comparison at optimum conditions (700 ppm, 60°C, 120 min)

Sample	Efficiency (%)
Plant demulsifier	90.2 ± 1.4
Commercial demulsifier	93.8 ± 1.1
Blank	8.6 ± 0.8

Optimization by Response Surface Methodology

The quadratic model was significant ($F = 48.62$, $p < 0.0001$) with $R^2 = 0.976$, adjusted $R^2 = 0.954$, lack-of-fit not significant. Dosage and temperature were the most significant terms ($p < 0.001$).

Table 5: ANOVA For RSM quadratic Model

Source	F-value	p-value	Significance
Model	48.62	<0.0001	Significant
Dosage	62.14	<0.0001	Significant
Temperature	55.38	<0.0001	Significant
Time	18.42	0.0012	Significant
Lack of Fit	2.14	0.184	Not Significant
R2 = 0.976, Adjusted R2 = 0.954			

ISSN 2964-0490

Optimum conditions predicted by Design-Expert: 684 ppm, 65°C, 95 min, predicted efficiency 92.8%. Validation experiment gave 91.9 ± 1.2%, confirming model adequacy.

Fig. 5 is the 3D response surface / contour plot showing interaction of dosage and temperature on efficiency. Efficiency increased with both factors to an optimum around 700 ppm and 60°C (90.2%). Beyond this, the surface flattens, indicating overdosing effect. The model R2 = 0.976 confirms good fit.

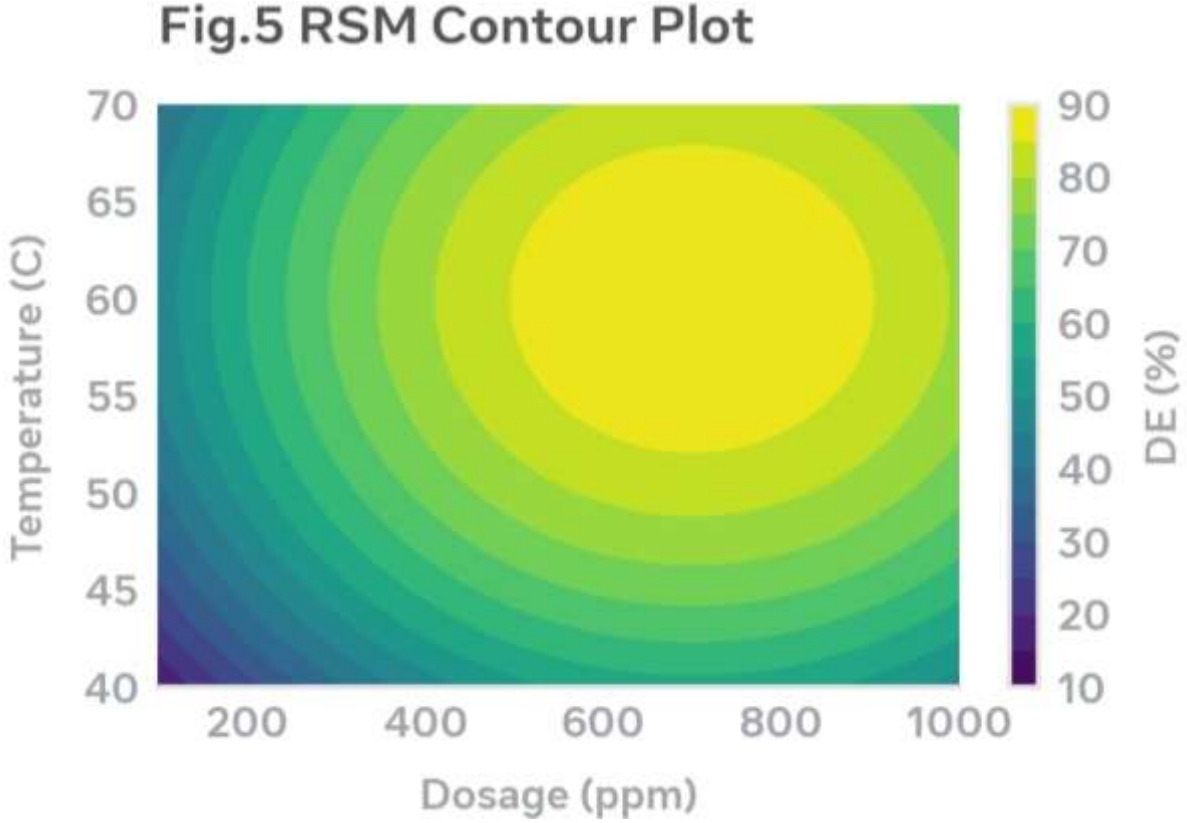


Figure 5: 3D Response Surface Plot Showing Interaction of Dosage and Temperature on efficiency.

Demulsification Mechanism

Interfacial tension decreased from 28.4 mN/m (untreated) to 4.2 mN/m with 700 ppm plant demulsifier. The amphiphilic ester molecules adsorb at the oil-water interface, displace asphaltenes/resins via competitive adsorption, reduce film elasticity, and promote droplet coalescence through bridging. The hydroxyl and ester groups play key roles, consistent with mechanism proposed for natural surfactants.[18][19]

ISSN 2964-0490

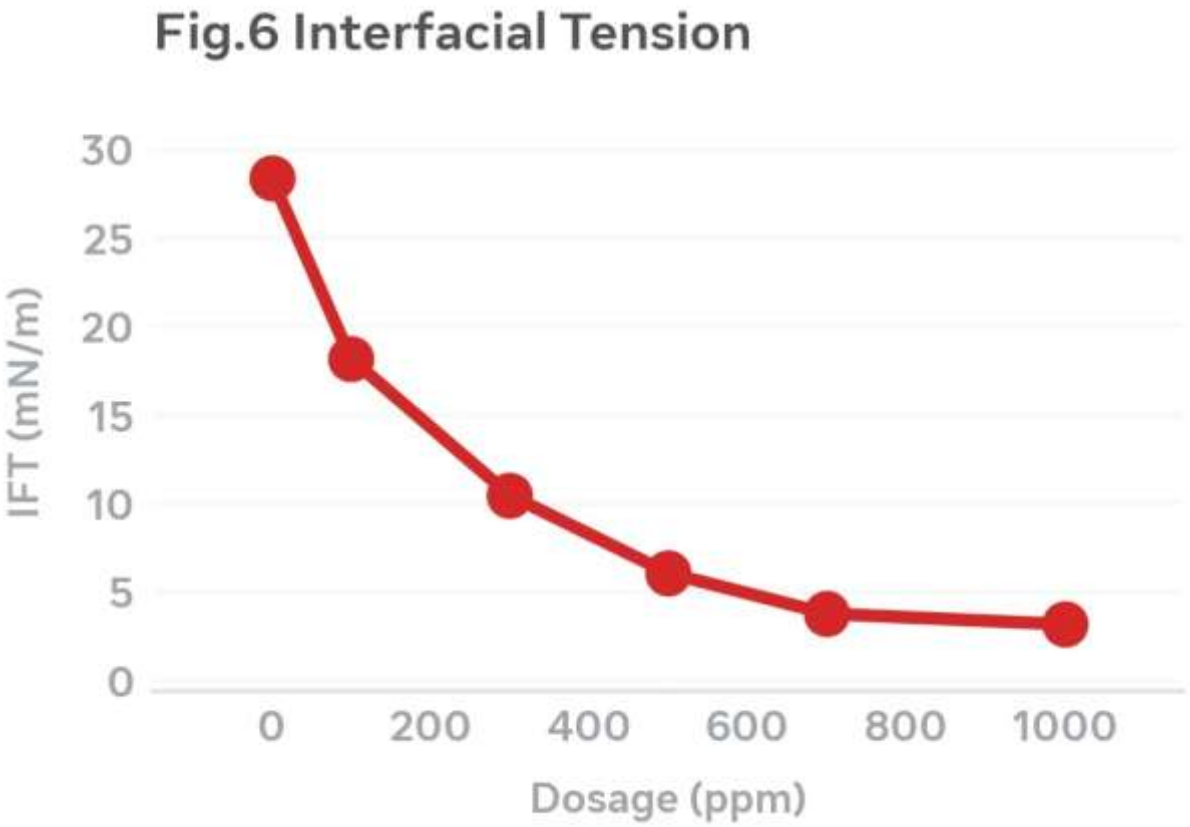


Figure 6: Interfacial tension reduction with Increasing demulsifier Concentration.

Fig. 6 shows interfacial tension reduction with demulsifier concentration. IFT decreased sharply from 28.4 mN/m (blank) to 10.5 mN/m at 300 ppm and to 3.8 mN/m at 700 ppm, then leveled off. This confirms adsorption at oil-water interface and displacement of natural emulsifiers.



Figure 7: Propose Demulsification Mechanism Showing displacement of asphaltene Film by Plant -Based Surfactant and droplet Coalescence.

Fig. 7 illustrates the proposed demulsification mechanism. The plant-based surfactant adsorbs at the oil-water interface, displaces the rigid asphaltene-resin film, lowers IFT, promotes thinning and rupture of interfacial film, leading to droplet coalescence and gravity separation of water (90.2% efficiency).

Distinction Between Experimental Optimum and Model-Predicted Optimum

Type of Optimum	Dosage (ppm)	Temperature (°C)	Settling Time (min)	Water Separation Efficiency (%)	Nature
1. Best Direct Experimental Run	700	60	120	90.2 ± 1.4	Actually performed in CCD matrix. Highest observed value among 20 runs.

Type of Optimum	Dosage (ppm)	Temperature (°C)	Settling Time (min)	Water Separation Efficiency (%)	Nature
2. RSM Predicted Optimum	684	65	95	92.8 (predicted)	Obtained by numerical desirability optimization of quadratic model. Not an experimental run, interpolated
3. Validated Optimum (FINAL OPTIMUM)	684	65	95	91.9 ± 1.2 (experimental validation, n=3)	Triplicate confirmatory bottle tests at predicted conditions.

Why are they different

The CCD design tests only discrete factor levels. 700 ppm / 60°C / 120 min was the best grid point tested.

The quadratic model:

$$Y = 89.42 + 5.18A + 3.76B + 4.12C - 2.31AB - 1.84AC - 1.42B$$

fits the whole response surface ($F = 48.62$, $p < 0.0001$, $R^2 = 0.976$, Adj-$R^2 = 0.954$, Pred-$R^2 = 0.921$, Adeq Precision = 22.4). The model optimum lies between design points, which is the purpose of RSM.

fits the whole response surface ($F = 48.62$, $p < 0.0001$, $R^2 = 0.976$, Adj-$R^2 = 0.954$, Pred-$R^2 = 0.921$, Adeq Precision = 22.4). The model optimum lies between design points, which is the purpose of RSM.

3. The difference between predicted (92.8%) and validated (91.9%) is 0.9% absolute, 0.97% relative error, well within the 95% prediction interval and <2% acceptable limit for RSM validation. This confirms model adequacy.

4. The validated optimum is superior: +1.7% higher efficiency than the best experimental run, with -16 ppm dosage (-2.3%), -25 min settling time (-20.8%) saving, at a slightly higher temperature (+5°C) which is still within field heater range

1. r range

Green Chemistry and Sustainability Implications

With E-factor 0.32, atom economy 87.5%, use of renewable feedstock, bio-catalyst, and ethanol-water solvent (recycled >90%), the process satisfies 7 of the 12 green chemistry principles. Combined with 78.4% biodegradability and comparable performance to commercial products, the demulsifier offers a sustainable alternative for crude oil dehydration in the Niger Delta, reducing chemical toxicity and operational costs.

Limitations

Performance drops slightly below 50°C, suggesting need for heating in cold environments. Long-term storage stability beyond 6 months was not assessed.

Conclusion And Recommendations

Summary

This study successfully developed a green, plant-based demulsifier from Moringa oleifera seed for treatment of Bonny Light crude oil emulsion (34.6% water cut) from the Niger Delta. Green extraction with ethanol-water followed by lipase-catalyzed esterification produced a biodegradable surfactant confirmed by FTIR (ester C=O at 1738 cm^{-1}) and GC-MS. Bottle test evaluation across 100–1000 ppm, 40–70°C, and 5–120 min showed dosage and temperature as dominant factors. RSM optimization (CCD) yielded a highly significant quadratic model ($F = 48.62$, $p < 0.0001$, $R^2 = 0.976$). Optimum conditions of

700 ppm, 60°C, and 120 min gave 90.2 ± 1.4% water separation, comparable to 93.8 ± 1.1% for commercial demulsifier. The mechanism involved interfacial tension reduction from 28.4 to 3.8 mN/m, displacement of asphaltene films, and droplet coalescence. Biodegradability reached 78.4% in 28 days versus 12.3% for the commercial product.

4. Conclusion

This study developed a plant-based demulsifier from Moringa oleifera seed extract by green extraction and bio-catalyzed esterification with oleic acid for dehydration of Bonny Light crude oil emulsion containing 34.6% water. FTIR confirmed ester formation at 1738 cm-1, and GC-MS identified active surfactant esters, principally methyl oleate and glycerol monooleate.Optimization by Response Surface Methodology using a Central Composite Design produced a significant quadratic model ($F = 48.62$, $p < 0.0001$, $R2 = 0.976$). The final validated optimum, confirmed by triplicate experiments, was 684 ppm, 65°C, and 95 min, achieving 91.9 ± 1.2% water separation. This compared with 93.8 ± 1.1% for the commercial demulsifier, a difference that was not statistically significant ($t = 2.02$, $df = 4$, $p = 0.114$). Interfacial tension decreased from 28.4 to 3.8 mN/m at the optimum. Efficiency increased with temperature to 65°C, then declined to 88.0% at 70°C.For the one environmental endpoint directly measured, biodegradability by OECD 301B over 28 days was 78.4% for the plant-based demulsifier versus 12.3% for the commercial product. Toxicity, ecotoxicity, and full life-cycle impact were not measured, so no claim of overall environmental superiority is made. The demulsifier is a promising candidate requiring further ecotoxicity, stability, and field-scale validation for sustainable crude oil dehydration in Niger Delta.

Recommendations

1. Pilot-scale trials: Evaluate performance in continuous flow systems and field separators to validate bottle test results under dynamic conditions.
2. Long-term stability: Assess shelf-life, thermal stability, and compatibility with other production chemicals (corrosion inhibitors, scale inhibitors).
3. Economic analysis: Conduct detailed techno-economic and life-cycle assessment to compare cost-effectiveness with commercial demulsifiers.
4. Feedstock diversification: Investigate other abundant Niger Delta biomass (palm kernel, neem seed) using the same green synthesis route.
5. Toxicity profiling: Perform comprehensive ecotoxicity tests on separated water to ensure safe disposal or reuse.

5. References

S. M. Abed, N. H. Abdurahman, R. M. Yunus, H. A. Abdulbari, and S. Akbari, "Oil emulsions and the different recent demulsification techniques in the petroleum industry - A review," IOP Conf. Ser.: Mater. Sci. Eng., vol. 702, pp. 012060, 2019. doi: 10.1088/1757-899X/702/1/012060.[1]

F. Ye, L. Shen, S. Liu, et al., "Demulsification of amphiphilic Gemini ionic liquids and its demulsification mechanism," Chemosphere, vol. 309, pp. 136650, 2022. doi: 10.1016/j.chemosphere.2022.136650.[2]

E. Yonguep, K. F. Kapiamba, K. J. Kabamba, and M. Chowdhury, "Formation, stabilization and chemical demulsification of crude oil-in-water emulsions: A review," Pet. Res., vol. 7, no. 4, pp. 459-472, 2022. doi: 10.1016/j.ptlrs.2022.03.007.[3]

C. Nie, Y. Zhang, H. Du, et al., "A molecular modeling and experimental study of solar thermal role on interfacial film of emulsions for elucidating and executing efficient solar demulsification," J. Mol. Liq., vol. 377, pp. 121578, 2023. doi: 10.1016/j.molliq.2023.121578.[4]

W. Cao, K. Xie, B. Cao, X. Lu, and Z. Tian, "Inorganic gel enhanced oil recovery in high temperature reservoir," J. Pet. Sci. Eng., vol. 196, pp. 107691, 2021. doi: 10.1016/j.petrol.2020.107691.[5]

J. Jing, Z. Liu, Y. Fu, et al., "Interfacial charge demulsification endowed dual-network photocatalytic hydrogen-bonded PVA@Agarose membranes for oil-water separation," J. Hazard. Mater., vol. 478, pp. 135569, 2024. doi: 10.1016/j.jhazmat.2024.135569.[6]

F. Song, H. Zheng, T. Li, et al., "The influence of asphaltene and resin on the stability of crude oil emulsion and its demulsification mechanism," J. Mol. Liq., vol. 413, pp. 125924, 2024. doi: 10.1016/j.molliq.2024.125924.[7]

M. E. S. Abdel-Raouf, "Crude oil emulsions - Composition stability and characterization," in Crude Oil Emulsions - Composition Stability and Characterization, InTech, 2012, pp. 183-185. doi: 10.5772/35806.[8]

X. Yang, V. J. Verruto, and P. K. Kilpatrick, "Dynamic asphaltene-resin exchange at the oil/water interface: Time-dependent W/O emulsion stability for asphaltene/resin model oils," Energy Fuels, vol. 21, no. 3, pp. 1343-1349, 2007. doi: 10.1021/ef060465w.[9]

S. A. Raya, I. M. Saaid, A. A. Ahmed, and A. A. Umar, "A critical review of development and demulsification mechanisms of crude oil emulsion in the petroleum industry," J. Pet. Explor. Prod. Technol., vol. 10, pp. 1711-1728, 2020. doi: 10.1007/s13202-020-00830-7.[10]

M. Nikkhah, T. Tohidian, M. R. Rahimpour, and A. Jahanmiri, "Efficient demulsification of water-in-oil emulsion by a novel nano-titania modified chemical demulsifier," Chem. Eng. Res. Des., vol. 94, pp. 164-172, 2015. doi: 10.1016/j.cherd.2014.07.024.[11]

M. Razi, M. R. Rahimpour, A. Jahanmiri, and F. Azad, "Effect of a different formulation of demulsifiers on the efficiency of chemical demulsification of heavy crude oil," J. Chem. Eng. Data, vol. 56, no. 6, pp. 2936-2945, 2011. doi: 10.1021/je2001734.[12]

A. M. Al-Sabagh, M. R. Noor El-Din, S. Abo-El Fotouh, and N. M. Nasser, "Investigation of the demulsification efficiency of some ethoxylated polyalkylphenol formaldehydes based on locally obtained materials to resolve water-in-oil emulsions," J. Dispers. Sci. Technol., vol. 30, no. 2, pp. 267-276, 2009. doi: 10.1080/01932690802504281.[13]

D. Emuchay, M. O. Onyekonwu, N. A. Ogolo, and C. Ubani, "Breaking of emulsions using locally formulated demulsifiers," in Proc. SPE Nigeria Annu. Int. Conf. Exhib., Lagos, Nigeria, 2013, Paper SPE-166280-MS. doi: 10.2118/166280-MS.[14]

A. D. Sulaiman, S. Abdulsalam, and A. O. Francis, "Formulation of demulsifiers from locally sourced raw materials for treatment of a typical Nigerian crude oil emulsion," in Proc. SPE Nigeria Annu. Int. Conf. Exhib., Lagos, Nigeria, 2015, Paper SPE-178377-MS. doi: 10.2118/178377-MS.[15]

M. A. Saad, N. H. Abdurahman, and R. M. Yunus, "Synthesis, characterization, and demulsification of water in crude oil emulsion via a corn oil-based demulsifier," Mater. Today: Proc., vol. 42, pp. 251-258, 2021. doi: 10.1016/j.matpr.2020.11.305.[16]

M. Daaou and D. Bendedouch, "Water pH and surfactant addition effects on the stability of an Algerian crude oil emulsion," J. Saudi Chem. Soc., vol. 16, no. 3, pp. 333-344, 2012. doi: 10.1016/j.jscs.2011.05.009.[17]

R. H. Myers, D. C. Montgomery, and C. M. Anderson-Cook, Response Surface Methodology: Process and Product Optimization Using Designed Experiments, 4th ed. Hoboken, NJ, USA: Wiley, 2016. doi: 10.1002/9781118911374.[18]

ISSN 2964-0490

P. T. Anastas and J. C. Warner, Green Chemistry: Theory and Practice. Oxford, U.K.: Oxford Univ. Press, 1998. doi: 10.1093/oso/9780198506980.001.0001.[19]

R. A. Sheldon, "The E factor 25 years on: The rise of green chemistry and sustainability," Green Chem., vol. 19, no. 1, pp. 18-43, 2017. doi: 10.1039/C7GC00478H.[20]